

COMPOSITE SOLID ELECTROLYTE FOR Li BATTERY APPLICATIONS

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ABSTRACT

The electrochemical, bulk and interracial properties of the polyethylene oxide (PEO) based polymer composite electrolyte (CSE) comprising LiI, PEO, and Al_2O_3 have been evaluated for Li battery applications. The bulk interfacial and transport properties of the CSEs seem to strongly dependent on the alumina particle size. For the CSE films with 0.05 micron alumina while the bulk conductivity is around 10^{-4} (mho cm⁻¹) at 103° C, the Li ion transport seems to be close to unity at the same temperature. Compared to the PEO electrolyte CSE seems to exhibit robust mechanical and interracial properties. We have studied three different films with three different alumina sizes in the range 0.01 - 0.3 micron. Effects of Al_2O_3 particle size on the electrochemical performance of the CSE films will be discussed. With TiS_2 as cathode a 10 mAh small capacity cell. was fabricated, charged and discharge] at C/40 and C/20 rates respectively.

INTRODUCTION

Recent activities in solid polymer electrolyte/Li batteries have centered around the use of polyethylene oxide (PEO) and other organic polymers complexed with lithium salts as the electrolyte. While considerable and significant advances have been made in terms of improving the bulk ionic conductivity and interracial properties of the polymeric electrolyte contacting Li(1) some basic and fundamental problems remain to be solved. The problems include: (a) Low transference number (0.1-0.3) for Li cations leading to high concentration polarization and high interface resistance, (b) Incompatible salt anions (BF_4^- , AsF_6^- , ClO_4^- , CF_3SO_3^- etc.) contained in the polymer that cause the lithium to degrade, and (c) Poor mechanical strength especially above 100°C . Other schools have used Al_2O_3 (2) or alumina based (3) to improve the mechanical strength of polymers. But, the lithium transference number was low because of an inappropriate salt, and too large Al_2O_3 particles. To overcome some of the shortcomings LiI was used in our studies. This salt is totally compatible with Li. The idea embodied in this work is to coat the alumina particles with a thin layer of LiI and to bond these particles together with PEO. It was expected that this composite solid electrolyte (CSE) would retain the vacancy conduction mechanism for Li^+ (responsible for near unity transference number of lithium) reported earlier (4) and in addition would exhibit the flexible nature of the polymer. In this study we report our

electrochemical. results on the CSE comprising LiI , PEO, Al₂O₃ and as a function of alumina particle size.

EXPERIMENTAL

Initially there were problems dispersing uniformly the Al₂O₃ particles in the PEO matrix. Thus a modified procedure, developed at the Jet Propulsion Laboratory, was adopted. Appropriate amounts of LiI , Al₂O₃, and PEO were weighed separately. LiI was dissolved in 50 ml of acetonitrile, decanted and to the solution was added alumina. The solution was stirred well for 45 minutes. 80 ml of Isopropyl alcohol (IPA) was added and the solution again was stirred well. To this mixture was added approximately 120 ml of acetonitrile followed by another 80 ml of IPA. While the solution was being stirred vigorously, 1.6 grams of PEO(M.W. 4×10^6) was added slowly. This procedure produced a uniform suspension of alumina in the solution. The mixture was stirred overnight to dissolve the PEO. This solution was cast into thin films as described elsewhere(5) . Our initial procedure to prepare thin films of CSE without the addition of IPA gave us only lumps of alumina covered with a coat of PEO. The thin films of CSE prepared by our modified procedure were subjected to a series of electrochemical measurements including a-c and d-c measurements. Both a symmetrical cell of the type Li/CSE/Li and an unsymmetrical cell of the type Li/CSE/SS (stainless steel) were used for the electrochemical characterization of the CSE films. With TiS₂ as the cathode a

small capacity cell was fabricated and charge/discharge studies were made.

RESULTS AND DISCUSSION

A) BULK CONDUCTIVITY AND INTERFACIAL CHARGE TRANSFER RESISTANCE:

Both the bulk conductivity ($1/R_b$) and the interfacial charge transfer resistance (R_{ct}) of the electrolyte (CSE) were determined from the a-c measurements. The a-c measurements were made in the frequency regime 100 kHz - 5 Hz. A typical Nyquist plot is shown in Figure 1 for CSE films containing 0.05 and 0.3 micron alumina. While the high frequency intercept on the x-axis is the bulk resistance of the electrolyte the corresponding low frequency intercept gives the combination of the bulk resistance of the interfacial layer (omnipresent on the I|J surface) and the charge transfer resistance, which we defined earlier as R_{ct} . The CSE film containing 0.3 micron Al_2O_3 exhibits three different regimes dominated by bulk processes at high frequencies followed by charge transfer processes at medium frequencies which in turn is followed by diffusional processes at low frequencies. However, the CSE films with 0.05 micron Al_2O_3 exhibits almost resistor like behavior where the contribution from the charge transfer and diffusional processes are insignificant. The a-c characteristics of the CSE films with 0.3 micron Al_2O_3 is typical of systems where the transport # of the reversible ion is very low. Hence we have not studied this material in depth. The behavior of CSE films with 0.01 micron Al_2O_3 is similar to that of 0.05 micron Al_2O_3

film. In the following we have described our results for CSE films with 0.05 Al₂O₃ only. In Figure 2 is shown the plot of the bulk conductivity of the CSE as a function of the reciprocal temperature. The data indicate that while the CSE exhibits a very modest conductivity below 79°C above this temperature the conductivity picks up. Further the temperature (79°C) at which the break occurs is higher than for PEO with out the alumina. For PEO system with out alumina the break in conductivity occurs around 60°C. The interracial charge transfer resistance appears to be stable over a period of many days.

B) TRANSPORT NUMBER

The transport numbers of the cation and anion represent the ratio of the total current that will be carried by the cations and anions respectively. When a uni-univalent salt comprising of two constituents M⁺ and X⁻ is dissolved in a solvent the salt dissociates into M⁺ and X⁻ in an ideal case. Under this condition the cation transport # corresponds to t₊ and the anion transport # is t₋. For the computation of the transport numbers we have made this assumption in our system. Several authors have developed different techniques to experimentally determine the transport number of the mobile ions(6). The simplest method developed by Sorensen and Jacobsen, involves identifying the contributions of different processes to the total conductivity by a-c measurement as a function of frequency in a symmetrical cell comprising two reversible electrodes separated by an electrolyte.

From the a-c results the transport number of the reversible ion can be computed as $t_+ = u_1/(u_1+u_2) = R_b/(R_b+Z_d)$ where u_1 and u_2 represent the mobility of positive and negative ions respectively and R_b is the bulk resistivity of the electrolyte and Z_d represents the impedance due to ion diffusion. This can be obtained as follows. The total impedance Z_t (comprising of $R_b+R_{ct}+Z_d$), of the system, is computed from the potentiodynamic measurement. From this total impedance, Z_t , subtracting R_b+R_{ct} gives Z_d . A-C and potentiodynamic measurements were made on the cells of the type Li/CSF/Li at 105°C. While R_b is close to 73 ohms R_{ct} and Z_d respectively are 2.5 and 2 ohms. The area of the electrolyte is very close to 1 cm². The cation transport number determined from these results is close to unity. This is a benchmark result that has not been reported in the literature yet. In Table-1 our electrochemical data are compared with the data available in the literature for comparable systems. The data indicate that not only the transport # is higher but the R_{ct} is lower for our system compared to state-of-the-art CSE systems.

C) THERMAL CREEP MEASUREMENT

The resistance of any material is directly proportional to its thickness. So by monitoring the resistance of the material as a function of time, in principle, at least qualitatively one can estimate the dimensional stability of the material using the formula $\text{creep}\% = (R-R_i)/R_i \times 100$ where $\text{creep}\%$ represents the percentage change in thickness and R_i and R respectively are the

initial resistance and resistance as a function of time. In Figure 3 we have shown a typical plot of creep% as a function of time for two different polymer electrolytes one containing alumina(CSE) and the other without. Our results indicate that this CSE is much more dimensionally stable than the PEO/LiI electrolyte.

D) STUDIES ON **Li/CSE/TiS₂** CELLS:

A 10 mAh small capacity cell was made with TiS₂ as a cathode and d-c cyclic voltammetric measurements were made as a function of open circuit voltages (OCVs). In Figure 4 is shown a typical d-c cyclic and in the same figure is shown the peak splitting as a function of OCV. The well defined cathodic and anodic peaks indicate that Li⁺ moves in and out of the TiS₂ cathode (the cell can be charged and discharged). The peak splitting increases with decrease in OCV of the cell. which may be related to the increase in resistance of TiS₂ with lithiation. In Figure 5 is shown the plot of diffusion coefficient of Li⁺ in TiS₂ as a function of OCV and charge transfer resistance at the TiS₂ electrode also as a function of OCV. While the R_{ct} varies randomly with OCV the diffusion coefficient goes through a maximum at around 50% state-of-charge. A similar observation was made earlier for TiS₂ cathode with organic electrolytes. In Figure 6 is shown the charge/discharge characteristics of the above cell. The cell was discharged at C/20 and charged at C/40 rates. Although the transport # for Li is close to unity the

charge/discharge rates are very low. One explanation would be that the CSE bulk ionic conductivity is still very low by an order of magnitude than the required minimum of 10^{-3} S cm⁻¹.

CONCLUSIONS

At the Jet Propulsion Laboratory we have developed a new chemical technique to disperse alumina uniformly in the high molecular weight PEO matrix. Our composite solid electrolyte (CSE) exhibits the highest transport number reported yet in the polymeric electrolyte for Li⁺. The conductivity of the CSE at 103°C is 1.0^{-4} mho cm⁻¹. Both the transport # and ionic conductivity are influenced by the particle size of alumina. Our thermal creep measurement studies show that the CSE is dimensionally stable much more than the PEO/LiI electrolyte. The cells could be charged and discharged only at very low rates although the cation transport # is very high.

ACKNOWLEDGEMENT

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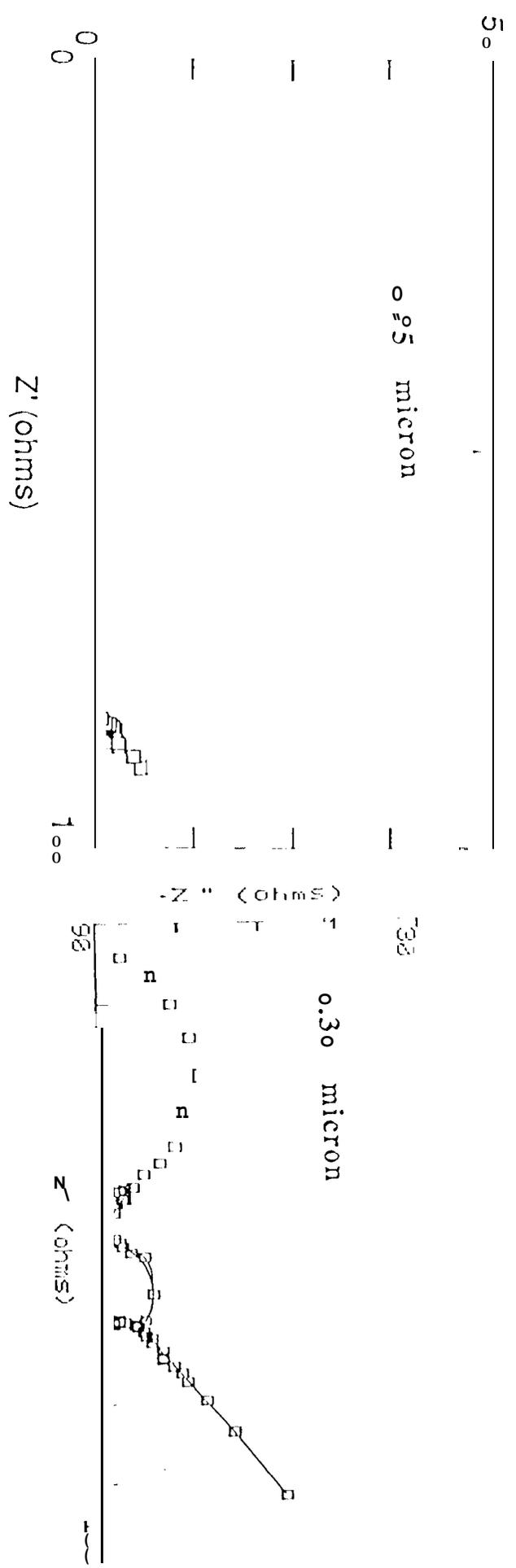
FIGURE CAPTIONS

- Fig. 1 Nyquist plot of the CSE
- Fig. 2 Conductivity vs. $1/T$ of the CSE
- Fig. 3 Creep% vs. Time of PEO/LiI with and with out Al_2O_3
- Fig. 4 D-C cyclic voltammetric characteristics of Li/CSE/ TiS_2 cell
- Fig. 5 Diffusion coefficient and R_{ct} vs. OCV.
- Fig. 6 Charge/discharge characteristics of Li/CSE/ TiS_2 cell

COMPARISON OF ELECTROCHEMICAL PROPERTIES OF CSE F LMS

Comp.	Temp. °C	Film bulk cond. mho cm ⁻¹	t _f	Interface resistance ohm cm ²
(F2U) (Al ₂ O ₃) ₃	116	6 × 10 ⁻⁴	0.8 ± 0.05	2.5
(Al ₂ O ₃) _{0.3}	90	0.0004	0.9 ± 0.05	20
(F2U) (Al ₂ O ₃) _{1.65}	103	10 ⁻⁴	1 ± 0.05	25
***** AR ⁺				
(F2U) (Al ₂ O ₃) ₃ *	120	3 × 10 ⁻⁴		
(F2U) (Al ₂ O ₃) ₂ *	110	10 ⁻⁴	0.22	25
(F2U) (Al ₂ O ₃) _{4.5} L15CN (6a)	115			

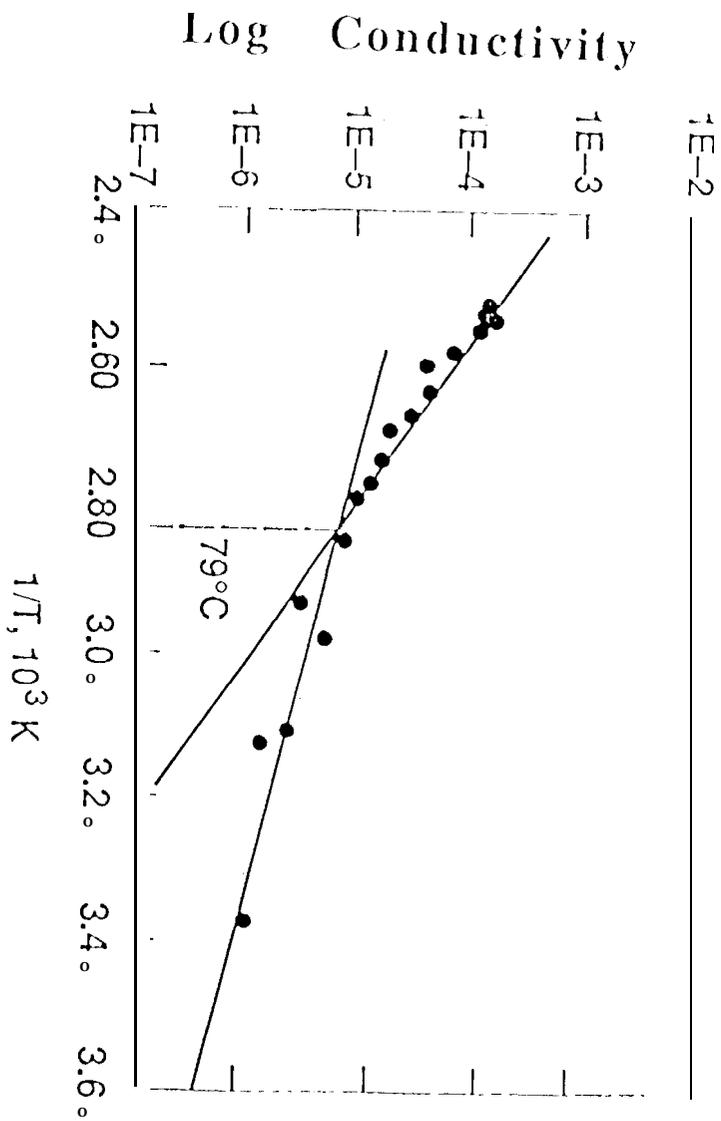
BUK CONDUCTIVITY AND TRANSFERENCE NUMBER OF THE CSES
EFFECT OF Al_2O_3 PARTICLE SIZE (0.05 MICRON / 0.3 MICRON $\alpha-Al_2O_3$)



COMPOSITE SOLID ELECTROLYTES

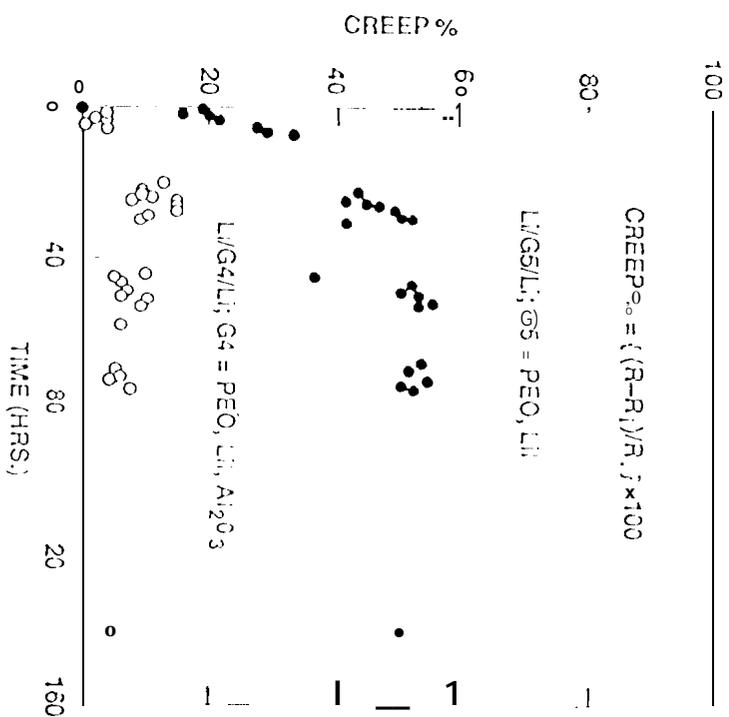
BULK CONDUCTIVITY VS. $1/T$

PEO+A 20g+10



CREEP MEASUREMENT AT 113°C

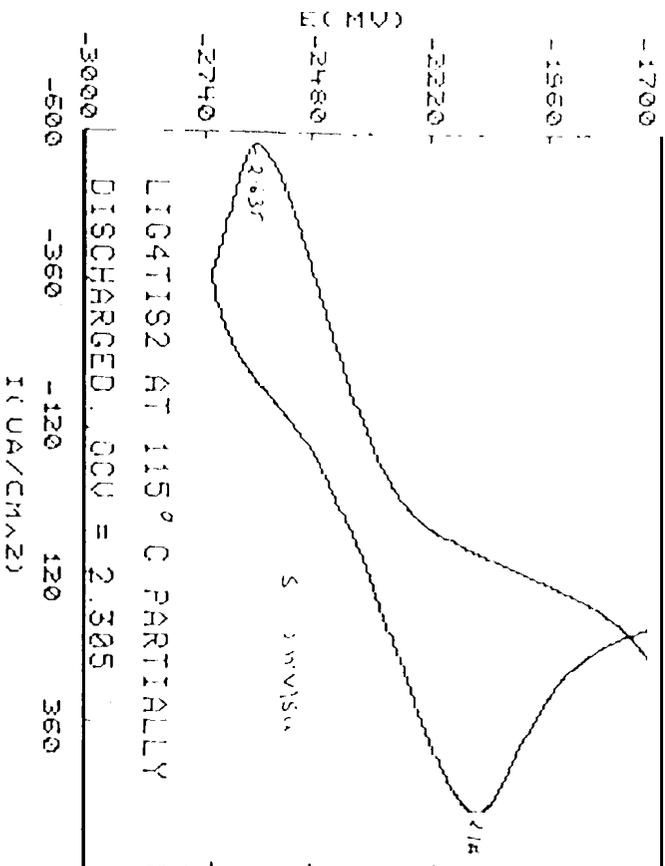
CREEP% vs. TIME



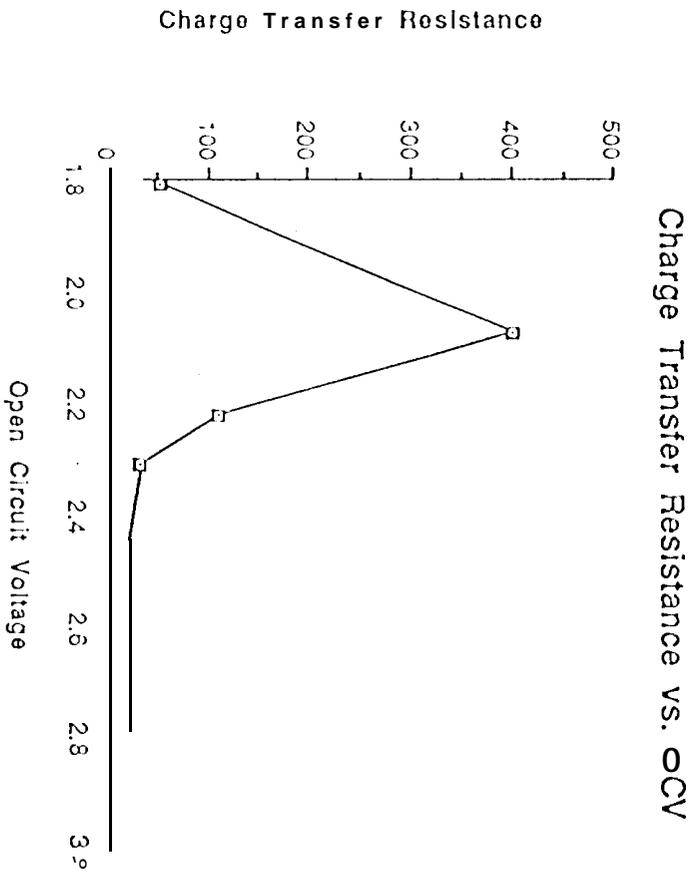
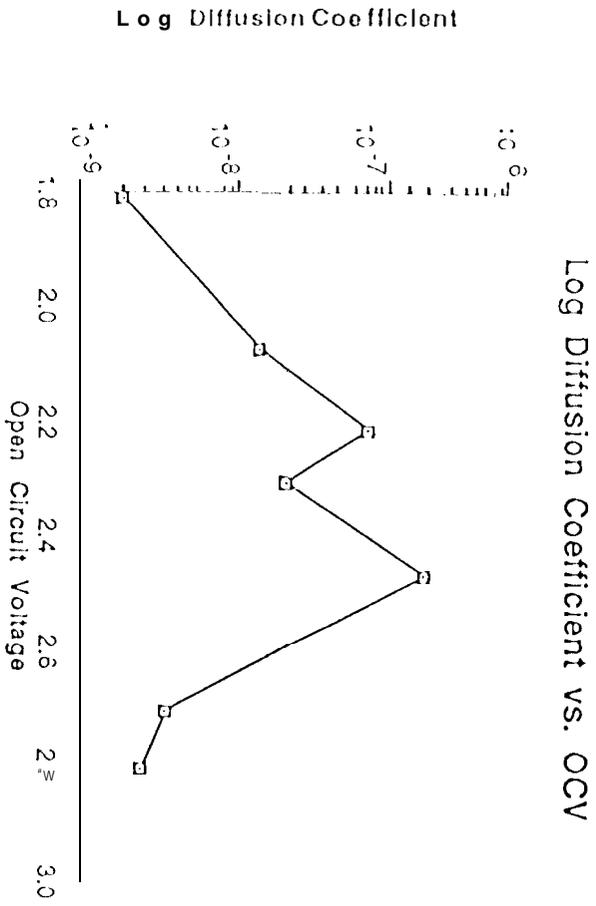
KINETIC PROPERTIES OF Li/CSE/TiS_2 AS A FUNCTION OF TEMP. AND SOC
 CATHODE CAPACITANCE 10 MAH
 D-C CYCLIC VOLTAMMETRIC CHARACTERISTICS

#	Temp ^o	Condition*	Initial OCV (V)	Anodic Peak Voltage V	Cathodic Peak Voltage V	V ₁ -V ₂
1	25	P.C. Fresh	2.27	2.13	2.625	0.495
2	115	P.D	2.305	2.108	2.63	0.522
3	115	P.D	2.215	2.087	2.688	0.601
4	115	P.C	2.215	2.087	2.688	0.601
5	115	P.C	2.215	2.087	2.688	0.601

* P.C. = Fully Charged; P.D. = Partially Charged; P.D
 Partially Discharged; P.D. = Fully Discharged.



DIFFUSION COEFFICIENT AND R_{ct} AS A FUNCTION OF SOC
 CELL CONFIGURATION: Li/CSE/TiS₂



CHARGE / DISCHARGE STUDIES

Li/CSE/TiS₂ (10 mAh)

